6.730 Physics for Solid State Applications

Lecture 22:

Outline

- Review of Effective Mass Theorem
- Impurity States in Semiconductors
- Fermi Surfaces in Metals
- Fermi Level, Chemical Potential
  - Intrinsic Semiconductors
  - Extrinsic Semicondutors

March 31, 2004

Summary Wavepacket properties

Without explicitly knowing the Bloch functions, we can solve for the envelope functions...

$$\left(E_n(-i\nabla_r) + \widehat{V}_{ext}(r)\right) \, G_n(r,t) = i\hbar \frac{\partial G_n(r,t)}{\partial t}$$

or $$\left(E_n(k_o - i\nabla_r) + \widehat{V}_{ext}(r)\right) \, F_n(r,t) = i\hbar \frac{\partial F_n(r,t)}{\partial t}$$

$$< r(t) >_G = \frac{< G_n(r,t)|r|G_n(r,t) >}{< G_n(r,t)|G_n(r,t) >} = < r(t) > \qquad < p >_G = \frac{< G_n(r,t)|\widehat{p}|G_(r,t) >}{< G_n(r,t)|G_n(r,t) >} \approx \hbar k_0$$

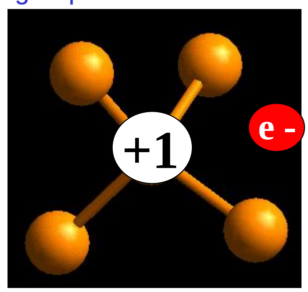
Semiclassical Equations of Motion:

$$\frac{d}{dt} < \mathbf{r}(t) > = < \mathbf{v_n}(\mathbf{k}) > = \frac{1}{\hbar}\nabla_{\mathbf{k}}\mathbf{E_n}(\mathbf{k})$$

$$\mathbf{F_{ext}} = \hbar\frac{\mathbf{dk}}{\mathbf{dt}}$$

Donor Impurity States
Example of Effective Mass Approximation

Replace silicon (IV) with group V atom...



$$V(\mathbf{r}) = \sum_{\mathbf{R}_\ell} \underbrace{V_{\mathrm{Si}}(\mathbf{r}-\mathbf{R}_\ell)}_{\text{periodic}} + \underbrace{\left[V_{\mathrm{As}}(\mathbf{r}) - V_{\mathrm{Si}}(\mathbf{r})\right]}_{\Phi_{\mathrm{ext}}(\mathbf{r})}$$

$$\Phi_{\mathrm{ext}}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_{\mathrm{Si}}}\frac{1}{|\mathbf{r}|}$$

Donor Impurity States
Example of Effective Mass Approximation

$$E_N(k) = E_c + \frac{\hbar^2(k-k_o)^2}{2m^*} + \ldots$$

$$\left(-\frac{\hbar^2\nabla^2}{2m^*} + E_c - \frac{e^2}{4\pi\epsilon|\mathbf{r}|}\right) F_N(r,t) = -\frac{\hbar}{i}\frac{\partial F_N(r,t)}{\partial t}$$

$$F_N(r,t) = F_N(r)e^{-iE_d t/\hbar}$$

This is a central potential problem, like the hydrogen atom...

$$\left(-\frac{\hbar^2\nabla^2}{2m^*} - \frac{e^2}{4\pi\epsilon|r|}\right) F_N(r) = (E_d - E_c)F_N(r)$$

$$E_l = E_d - E_c = -\frac{m^* e}{2(4\pi\epsilon)^2\hbar^2 l^2} = -\frac{13.6}{l^2}\left(\frac{m^*}{m}\frac{\epsilon_0^2}{\epsilon^2}\right)\ \text{eV}$$

with $\quad l = 1, 2, 3, 4, \ldots$

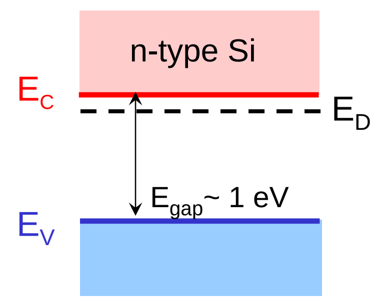
Donor Impurity States
Example of Effective Mass Approximation

Hydrogenic wavefunction with an equivalent Bohr radius..

$$F_1(r) = Ae^{-r/r_0} \qquad \text{where} \qquad r_0 = \frac{\epsilon\hbar^2}{m^* e^2} = \epsilon\frac{m}{m^*}(0.53\,\text{A})$$

Donor ionization energy...

$$E_d = E_c - \frac{13.56}{l^2\epsilon^2}\frac{m^*}{m}\ \text{eV}$$



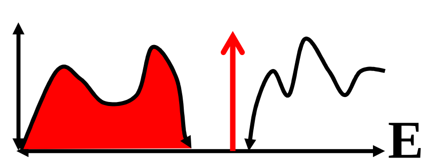
There are an infinite number of donor energies, E_D is the lowest energy with l=1, and from Statistical Mechanics we will see it is the most important one...

Donor Impurity States
Example of Effective Mass Approximation

$$g(E) = g_{\text{Si}}(E) + \sum_l g_l \delta(E - E_l)$$

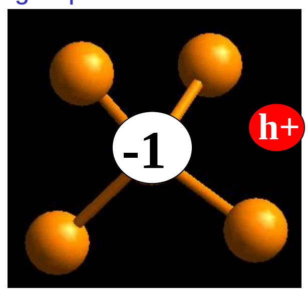
When there are N_d donor impurities...

$$g(E) = g_{\text{Si}}(E) + N_d \sum_l g_l \delta(E - E_l)$$



Acceptor Impurity States
Example of Effective Mass Approximation

Replace silicon (IV) with group III atom...



$$V(\mathbf{r}) = \sum_{\mathbf{R}_\ell} \underbrace{V_{\mathrm{Si}}(\mathbf{r}-\mathbf{R}_\ell)}_{\text{periodic}} + \underbrace{\left[V_{\mathrm{B}}(\mathbf{r}) - V_{\mathrm{Si}}(\mathbf{r})\right]}_{\Phi_{\text{ext}}(\mathbf{r})}$$

$$\Phi_{\text{ext}}(r) = \frac{e^2}{4\pi\epsilon}\frac{1}{|r|}$$

Acceptor Impurity States
Example of Effective Mass Approximation

$$E(k) = E_v - \frac{\hbar^2 k^2}{2m^*} + \dots$$

$$\left(E_v + \frac{\hbar^2\nabla^2}{2m^*} + \frac{e^2}{4\pi\epsilon|r|}\right) F_N(r,t) = -\frac{\hbar}{i}\frac{\partial F_N(r,t)}{\partial t}$$

$$G_N(r,t) = G_N(r)e^{-iE_a t/\hbar}$$

Another central potential problem...

$$\left(-\frac{\hbar^2\nabla^2}{2m^*} - \frac{e^2}{4\pi\epsilon|r|}\right) F_N(r) = (E_v - E_a)F_N(r)$$

$$E_l = E_v - E_a = -\frac{m^* e}{2(4\pi\epsilon)^2\hbar^2 l^2} = -\frac{13.6}{l^2}\left(\frac{m^*}{m}\frac{\epsilon_0^2}{\epsilon^2}\right)\ \text{eV}$$

with $l = 1, 2, 3, 4, \dots$

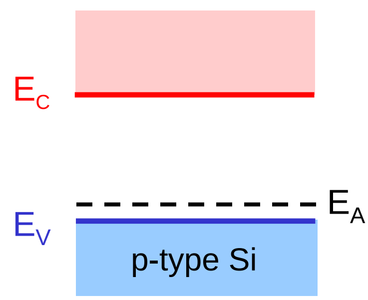
Acceptor Impurity States
Example of Effective Mass Approximation

Hydrogenic wavefunction with an equivalent Bohr radius..

$$F_1(r) = Ae^{-r/r_0} \qquad \text{where} \qquad r_0 = \frac{\epsilon\hbar^2}{m^* e^2} = \epsilon\frac{m}{m^*}(0.53\,\text{Å})$$

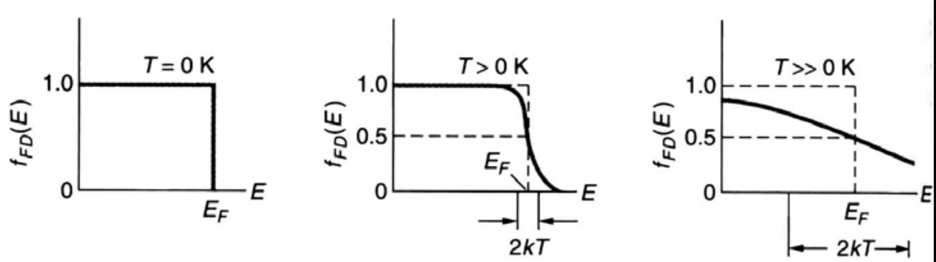
Acceptor ionization energy...

$$E_a = E_v + \frac{13.56}{l^2\epsilon^2}\frac{m^*}{m}\ \text{eV}$$



There are an infinite number of acceptor energies, E_A is the lowest energy with l=1, and from Statistical Mechanics we will see it is the most important one

Finite Temperatures: Where in the world is the Fermi Energy?
$E_F(T) = \mu(T)$



$$n = \frac{N}{V} = \int_{-\infty}^{\infty} \frac{1}{1+e^{(E_{\mathbf{k}}-\mu)/k_BT}}\, 2\frac{d^3\mathbf{k}}{(2\pi)^3}$$

$$n = \int_{-\infty}^{\infty} \frac{1}{1+e^{(E-\mu)/k_BT}}\, g(E)\, dE$$

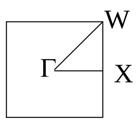
μ is found from the integral equation given that n is fixed.

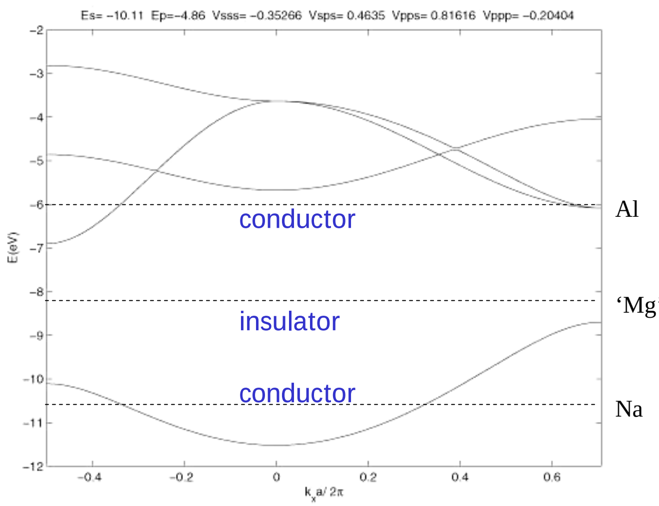
1. A metal: If μ is in the bands
2. A semiconductor: if μ is in the gap and gap > kT
3. Semimetal: if m is in the gap and gap is of the order of kT

2D Monatomic Square Crystals

Dispersion Relations

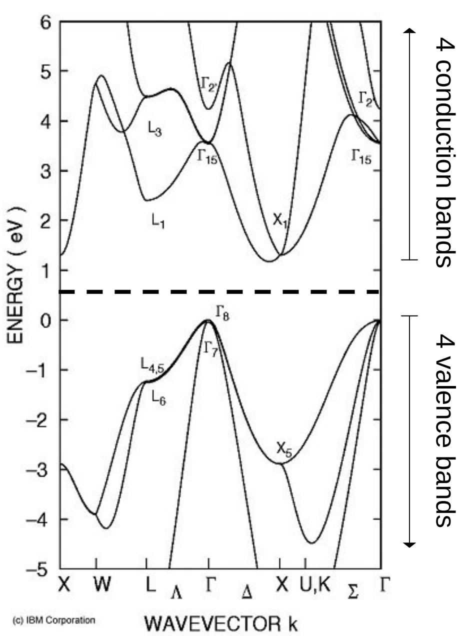
a = 5.5 A





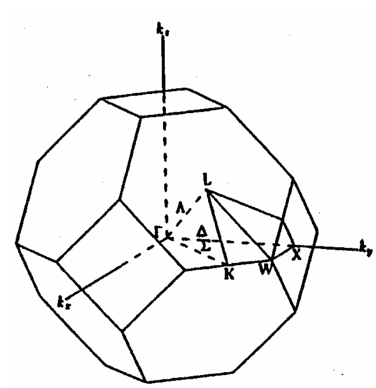
I	II	III	IV	V	VI	VII	VIII
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

Silicon Bandstructure



Si: [Ne] $3s^2\,3p^2$

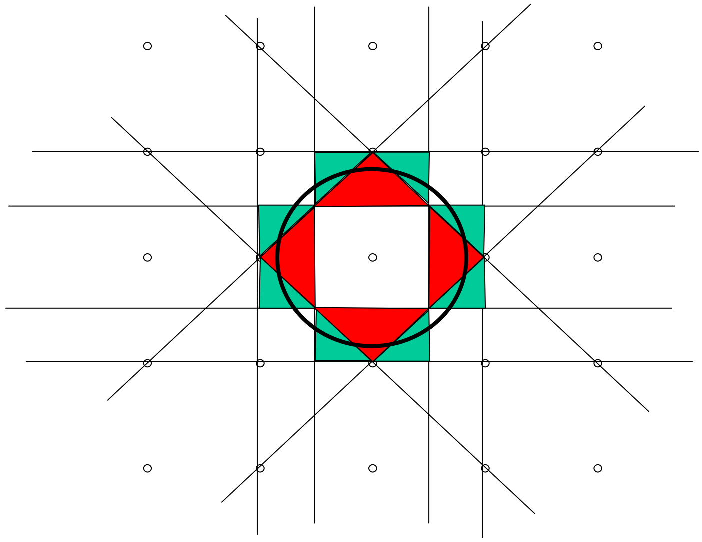
4 e- per silicon atom
2 silicon atoms per lattice site
total: 8 electrons at each site



Metasl: Free Electron Fermi Surfaces (2D)

T=0

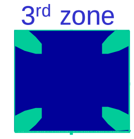
For free electrons energy surfaces are simple spheres (circles)…
Valence (# of electrons) determines radius of energy surface…



1st zone

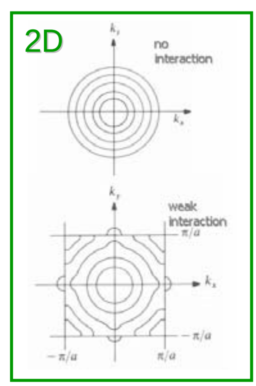
2nd zone

3rd zone

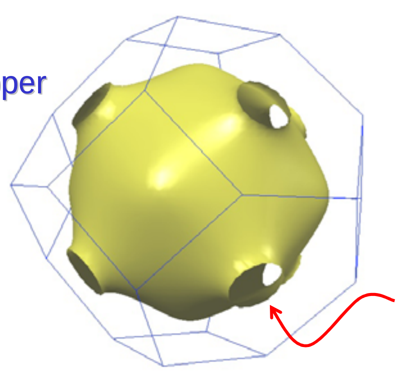


Fermi Surfaces (3D)

When k near to BZ boundary:
⇨ E contours become distorted



copper

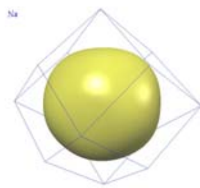


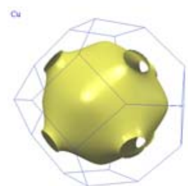
periodic potential pulls on the spherical FS forming 'necks'

www.phys.ufl.edu.fermisurface

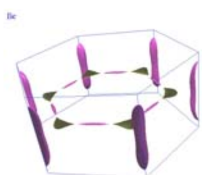
Fermi Surfaces (3D)

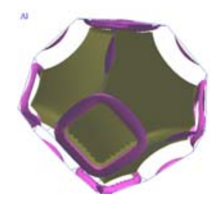
N_e = 1 monovalent metals, e.g. Na, Cu, with values ~ f.e. theory





other cases, e.g. Be (N_e=2), Al (N_e=3), there are serious differences

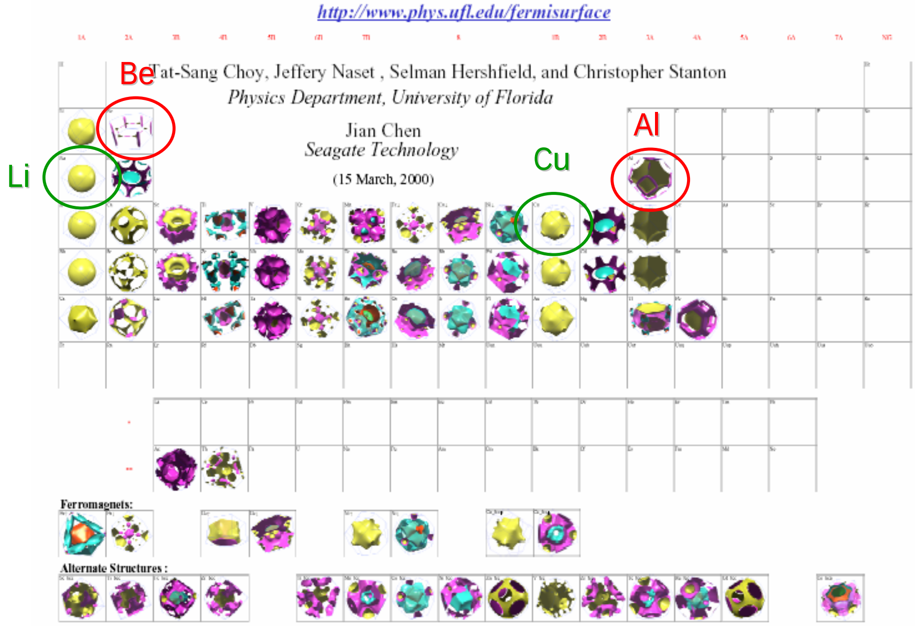




www.phys.ufl.edu.fermisurface

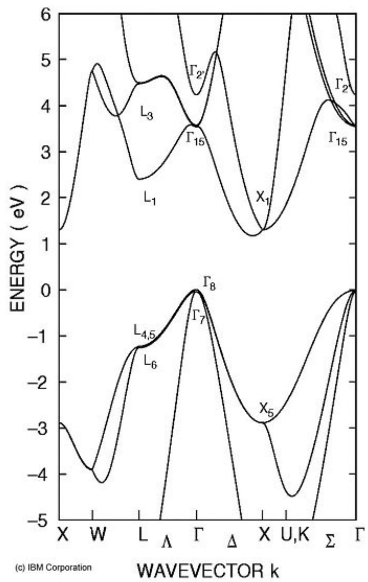
Periodic Table of the Fermi Surfaces of Elemental Solids

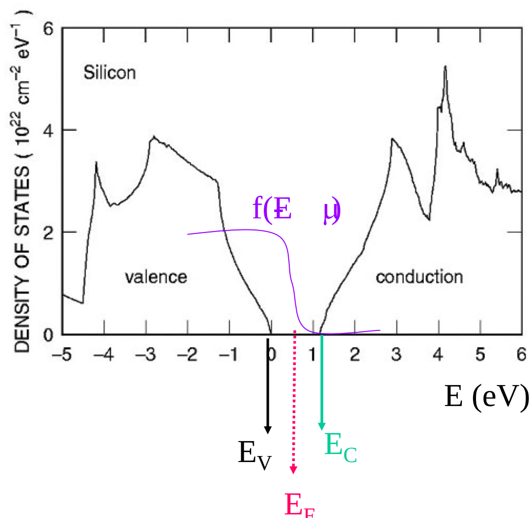
http://www.phys.ufl.edu/fermisurface



Source of tight binding parameters (except for fcc Co ferromagnet): D.A. Papaconstantopoulos, *Handbook of the band structure of elemental solids*, Plenum 1986.
This work is supported by NSF, AFOSR, Research Corporation, and a Sun Microsystems Academic Equipment Grant.

Semiconductors: Silicon Bandstructure





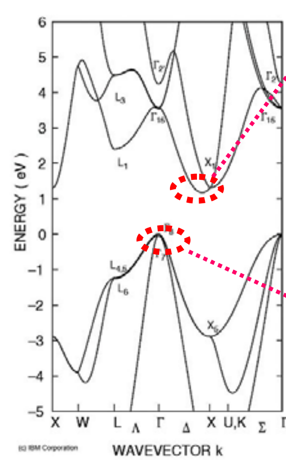
The fermi “tails” are in the conductions and valence bands

http://www.research.ibm.com/DAMOCLES/html_files/phys.html

Density of State Effective Mass (3D)

Ellipsoidal Energy Surfaces

Silicon energy surfaces can often be approximate as near the top or bottom as



A. For each of the 6 conduction “pockets”

$$E_N(k) = E_c + \frac{\hbar^2}{2}\left(\frac{(k_x - k_x^0)^2}{m_t} + \frac{(k_y - k_y^0)^2}{m_t} + \frac{(k_z - k_z^0)^2}{m_l}\right)$$

$$g_c = \frac{\sqrt{2}}{\pi^2 \hbar^3}(m_{\mathrm{dc}}^*)^{3/2}\sqrt{E - E_c}$$

where the density of states effective mass is

$$m*_{\mathrm{dc}} = (m_t m_l m_l)^{1/3}$$

B. For each of the valence bands

$$E_N(k) = E_v - \frac{\hbar^2}{2m_i}k^2$$

i = light hole and heavy hole

$$g_v = \frac{\sqrt{2}}{\pi^2 \hbar^3}(m_i^*)^{3/2}\sqrt{E_v - E}$$

for each of the valence bands

http://csmr.ca.sandia.gov/workshops/nacdm2002/viewgraphs/Conor_Rafferty_NACDM2002.pdf

To find the Fermi Level of the Semiconductor

The number of particles thermally excited to the conduction band n_C must equal the number of electron vacancies in the valence band p_V so that charge neutrality is preserved.

$$n_c = \int_{-\infty}^{\infty} \frac{1}{1+e^{(E-\mu)/k_BT}} 6g_c(E)\,dE$$

$$p_v = \int_{-\infty}^{\infty} \left[1 - \frac{1}{1+e^{(E-\mu)/k_BT}}\right] \left(\sum_i g_{vi}(E)\right) dE$$

Solving for $n_C = p_V$ give the fermi level (chemical potential) $\mu(T)$

Counting and Fermi Integrals

3-D Conduction Electron Density

$$n = \int_{E_c}^{\infty} 6g_c(E)f(E)dE \qquad g_c(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E-E_c}$$

$$n = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\int_{E_c}^{\infty}\frac{\sqrt{E}}{1+\exp\left(\frac{E-\mu}{k_BT}\right)}dE$$

$$= \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\int_{E_c}^{\infty}\frac{\sqrt{y}\sqrt{k_BT}}{1+e^{y-v}}k_BT dy \qquad y = \frac{E-\mu}{k_BT}$$

$$= \frac{2}{\sqrt{\pi}}2\left(\frac{m^*k_BT}{2\pi\hbar^2}\right)^{3/2}\int_0^{\infty}\frac{\sqrt{y}}{1+e^{y-v}}dy \qquad v = \frac{\mu-E_c}{k_BT}$$

$$\boxed{n = \frac{2}{\sqrt{\pi}}N_c F_{1/2}\left(\frac{\mu-E_c}{k_BT}\right)}$$

Counting and Fermi Integrals

3-D vacancy Density

$$p = \int_{-\infty}^{E_v} (\sum_i g_{vi}(E))(1 - f(E))dE$$

$$p_{hh} = \frac{2}{\sqrt{\pi}} 2 \left(\frac{m_{hh}^* k_B T}{2\pi\hbar^2}\right)^{3/2} F_{1/2}\left(\frac{E_v - \mu}{k_B T}\right) \quad p_{lh} = \frac{2}{\sqrt{\pi}} 2 \left(\frac{m_{lh}^* k_B T}{2\pi\hbar^2}\right)^{3/2} F_{1/2}\left(\frac{E_v - \mu}{k_B T}\right)$$

$$m_{hh}^*|_{\text{GaAs}} = 0.51\, m \qquad m_{lh}^*|_{\text{GaAs}} = 0.087\, m$$

$$\frac{p_{lh}}{p_{hh}} = \left(\frac{m_{hh}^*}{m_{lh}^*}\right)^{3/2} \approx \left(\frac{0.51}{0.87}\right)^{3/2} = 13.7$$

$$p = \frac{2}{\sqrt{\pi}} 2 \left(\frac{m_v^* k_B T}{2\pi\hbar^2}\right)^{3/2} F_{1/2}\left(\frac{E_v - \mu}{k_B T}\right)$$

$$(m_v^*)^{3/2} = (m_{hh}^*)^{3/2} + (m_{lh}^*)^{3/2}$$

$$\boxed{p = \frac{2}{\sqrt{\pi}} N_v F_{1/2}\left(\frac{E_v - \mu}{k_B T}\right)}$$

Boltzmann Approximation

Boltzmann Approximation: $F_{1/2}(v) \approx \frac{\sqrt{\pi}}{2} e^v$

$$n_o = \frac{2}{\sqrt{\pi}} N_c F_{1/2}\left(\frac{E_{F_o} - E_c}{k_B T}\right) \rightarrow N_c \exp\left(\frac{-(E_c - E_{F_o})}{k_B T}\right)$$

$$p_o = \frac{2}{\sqrt{\pi}} N_v F_{1/2}\left(\frac{E_v - E_{F_o}}{k_B T}\right) \rightarrow N_v \exp\left(\frac{-(E_{F_o} - E_v)}{k_B T}\right)$$

Intrinsic carrier concentration with n = p

$$n_o p_o = N_c N_v \exp\left(\frac{-(E_c - E_v)}{k_B T}\right) = N_c N_v \exp\left(\frac{-E_g}{k_B T}\right) = n_i^2$$

Intrinsic Fermi level

$$E_{Fo} = E_i = \frac{E_c + E_v}{2} + \frac{k_B T}{2} \ln \frac{N_v}{N_c}$$

Electronic Specific Heat of the Semiconductor

The particles thermally excited to the conduction band n_C must gain an energy of about $E \quad E_C$

$$\Delta E = \int_{-\infty}^{\infty} \frac{1}{1+e^{(E-\mu)/k_BT}} \, 6g_c(E)\,(E-E_c)\,dE$$

$$\Delta E \approx n_i(T)\,E_g = \frac{\sqrt{2}}{\pi} N_c(T) e^{-E_g/2k_BT}\, E_g$$

$$C_v \approx \frac{\sqrt{2}}{\pi} N_c(T)\, \frac{E_g^2}{2k_BT^2}\, e^{-E_g/2k_BT}$$

Electronic Specific heat decreases exponentially fast with T at low T; in contrast, a metal decrease linearly with T.

Doped Semiconductors

The fermi level is again found from Charge Neutality

$$p - n + N_D^+ - N_A^+ = 0$$

Density of “ionized” donors

Density of “ionized” acceptors

Use the fact that even for doped materials, in the Boltzman limit,

$$n = \frac{2}{\sqrt{\pi}} N_c F_{1/2}\left(\frac{E_F - E_c}{k_BT}\right) \to N_c \exp\left(\frac{-(E_c - E_F)}{k_BT}\right)$$

$$p = \frac{2}{\sqrt{\pi}} N_v F_{1/2}\left(\frac{E_v - E_F}{k_BT}\right) \to N_v \exp\left(\frac{-(E_F - E_v)}{k_BT}\right)$$

$$np = N_c N_v \exp\left(\frac{-(E_c - E_v)}{k_BT}\right) = N_c N_v \exp\left(\frac{-E_g}{k_BT}\right) = n_i^2$$

Extrinsic Semiconductors

For high temperatures where all the donors and acceptors are ionixed,

$$\frac{n_i^2}{n} - n + N_D - N_A = 0$$

Therefore, in the Boltzman (extrinsic) limit,

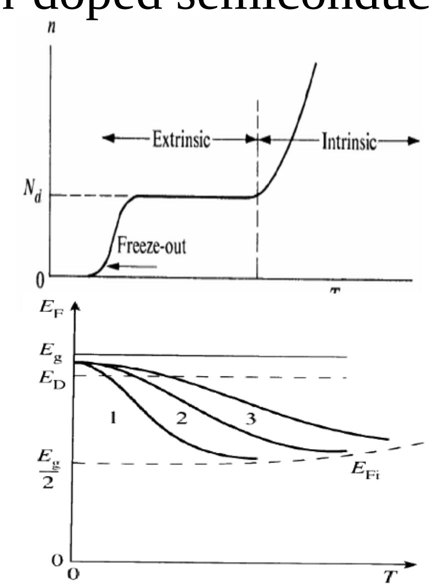
$$n = \frac{N_D - N_A}{2} + \left[\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2\right]^{1/2}$$

For n doped materials, $N_D \gg N_A$ and $N_D \gg n_i$

$$n \approx N_D \quad \text{and} \quad p = n_i^2/N_D$$

We aslo find that $E_F = E_i + k_B T \ln \frac{N_D}{n_i}$

n-doped semiconductor



http://www.physics.fsu.edu/courses/Spring04/phz3400/notes/semicon1.pdf

Approximations for Fermi Integrals

3-D Carrier Densities

$$N_o = \frac{2}{\sqrt{\pi}} N_c\, F_{1/2}\left(\frac{E_{F_o} - E_c}{k_B T}\right) = \frac{2}{\sqrt{\pi}} N_c\, F_{1/2}\,(v) \qquad\qquad v = \frac{E_{F_o} - E_c}{k_B T}$$

Sommerfeld Approximation:

$$F_{1/2}\,(v) \approx \frac{2}{3} v^{3/2}\left[a_1 + a_2 v^{-2} + \ldots\right]$$

$$a_1 = 1 \qquad\qquad a_2 = \frac{\pi^2}{8} \approx 1.2337$$

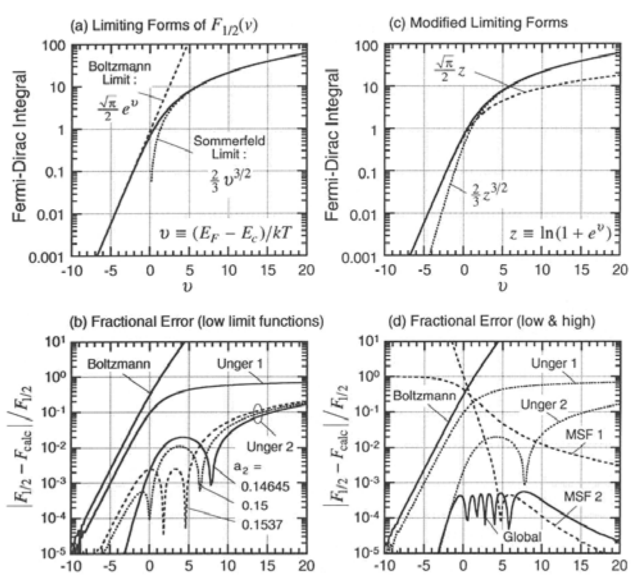
Unger Approximation:

$$F_{1/2}\,(v) \approx \frac{\sqrt{\pi}}{2} z\left[a_1 + a_2 z + \ldots\right] \quad \text{where} \quad z = \ln\left(1 + e^{v}\right)$$

$$a_1 = 1 \qquad\qquad a_2 = \frac{1}{2}\left(1 - \frac{1}{\sqrt{2}}\right) \approx 0.14645$$

Approximations for Fermi Integrals

3-D Carrier Densities



Approximations for Inverse Fermi Integrals

$$r = \frac{N}{N_c} \qquad v = \frac{E_{F_o} - E_c}{k_B T}$$

Inverse First-order Sommerfeld Approximation:

$$v \approx \left(\frac{3\sqrt{\pi}}{4} r\right)^{3/2} \qquad v > 20$$

for 0.04 error

Inverse Second-order Unger Approximation:

$$v \approx \ln(\exp(\frac{1}{2a_2}(\sqrt{1 + 4a_2 r} - 1)) - 1)$$

$$a_2 = 0.146545 \qquad v < 2.8$$

$$a_2 = 0.15 \qquad v < 7.4$$

for 0.04 error